Bulletin of Electrochemistry 15 (9-10) September-October 1999, pp 394-399

0256-1654/99/$ 3-50

PLATINUM ALLOY BIMETALLIC CATALYSTS FOR FUEL CELLS

R PATTABIRAMAN

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

Bimetallic alloy catalysts of Pt-Pd, Pt-Ru, Pd-Ru and Pd-Ag were prepared at 5 and 10 wt.% loading at different atomic compositions on carbon supports. The catalysts were subjected to a heat treatment at 923 K in hydrogen atmosphere. The catalysts were characterised by XRD and electrochemical techniques. Porous carbon electrodes were fabricated and the electrocatalytic activity towards electrooxidation of methanol, formaldehyde and ethylene glycol in acid and alkaline solutions were evaluated.

Keywords: Pt and Pd alloy catalysts, carbon supports, electrooxidation of methanol, formaldehyde and ethylene glycol.

INTRODUCTION

It is now widely accepted that Pt and Pt group alloys are the only suitable catalyst materials for the electrochemical reactions in fuel cells with acidic or alkaline electrolytes operating at temperatures below 483 K [1-3]. Studies on binary or tertiary metals, or alloy surfaces and bimetallic combinations have in the last few years gained increased attention as oxygen reduction electrocatalysts in phosphoric acid fuel cells [4-8], polymer membrane electrolyte fuel cells [9], alkaline fuel cells or for direct electrochemical oxidation of methanol [11]. These catalysts, which are composed of Pt-M surface dispersed on high surface area carbon supports, where M denotes a 3-d transition metal e.g. Ti, Cr, Fe, Co, Cu etc. have shown enhanced catalytic activities and stable electrochemical properties. It has been suggested that the surface roughness due to dissolution of the transition metals in acid gives high surface area effects resulting in significant increase in the oxygen reduction reaction [6,9].

The electrooxidation of methanol has been suggested to proceed via the oxidation of the adsorbed intermediate COH. The catalyst provides sites for the adsorption of OH radicals and facilitates the oxidation of the intermediate. A number of bimetallic catalyst systems have been reported for the oxidation of methanol and its intermediates [12,13]. Amongst them the Pt-Sn [14-16], Pt-Ru-Sn [17] and Pt-Ru [18-21] are the most widely studied materials. The studies have revealed that Pt-Ru are the best candidate materials for oxidation of CH_3OH.

Recently Pd base alloys have also been reported as catalysts for the electroreduction of oxygen [22] and electrooxidation of ethylene glycol [23]. However, the detailed studies on other fuels are not reported. In this connection, an attempt has been made to prepare Pt-Ru, Pd-Ru, Pt-Pd and Pd-Ag catalysts on carbon supports to study their electrocatalytic activity for the oxidation of methanol, formaldehyde and ethylene glycol and the results are discussed in this paper.

EXPERIMENTAL

Preparation of catalysts on carbon supports

Activated charcoal (BET surface area = 322 m^2/g) was used as the catalyst support. Pt, Ru, Pd salts from M/s. Arora Mathey Ltd., India were used. Catalysts (5 and 10 wt.%) were prepared by incipient dry technique followed by reduction in hydrogen at 673 K and by chemical reduction methods [24]. The catalysts were heat treated in hydrogen atmosphere at 873 K for 1 hr.

Characterisation of catalysts

The XRD patterns were obtained in a JEOL X-RAY Diffractometer Model 8030 using a CuK_α radiation. The crystallite parameters, like crystallite size (C_s), the Metal Surface Area (MSA) and the dispersion (D in%) i.e. the ratio of number of surface atoms to the bulk were evaluated as per known procedures [25,26]. Porous carbon electrodes were fabricated as per the procedure described in previous publications [27,28]. The catalyst loading was kept at a value of 2 mg/cm^2.

TABLE I: Characteristics from XRD data

Catalyst	Method	Atom (%)	Atom (%)	Crystallite size (nm)	MSA (m^2/g)	D (%)	Lattice const a_0 in nm
Pt-Pd	incipient	50	50	6.00	46.60	17.00	0.3911
Pt-Ru	"	50	50	13.06	23.00	8.50	0.3906
Pd-Ru	"	50	50	15.96	17.50	6.50	0.3895
Pd-Ag	"	50	50	23.40	11.02	6.70	0.4001
Pt-Pd	chemical	50	50	4.80	58.30	21.00	
Pt-Ru	"	50	50	19.80	28.20	11.00	0.3901
Pd-Ru	"	50	50	20.27	12.80	5.30	0.3906
Pd-Ru	heat treated	50	50	26.60	10.30	4.10	0.3910
Pd-Ag	chemical	50	50	11.20	22.02	8.60	0.4006

Electrochemical studies

The electrochemical surface area values (ESA) were evaluated from the charge involved in the oxidation of adsorbed hydrogen in the potential range 50-400 mV from the cyclic voltammograms in 1.0 *M* H_2SO_4 solution, assuming a charge value of 210 $\mu C/cm^2$ for a monolayer coverage [29]. The electrocatalytic activity measurements were carried out in both 1.0 *M* H_2SO_4 and in 1.0 *M* KOH solutions. SCE and mercuric oxide electrodes (MOE) were used as reference electrodes in the respective electrolytes. A Pt foil was used as the counter electrode. Steady state galvanostatic polarisation studies were carried out at 308 K for the anodic oxidation of methanol, formaldehyde and ethylene glycol (1.0 *M*) in both the medium.

RESULTS AND DISCUSSION

Analysis of XRD data

The XRD pattern obtained for the various Pt-Ru binary catalyst systems have been reported earlier in detail [28, 30]. Both Pt and Pd are known to form a complete substitution solid solution of the FCC lattice at all composition ranges. The overlapping of the reflections from 111, 200 and 220 planes occur for the different Pt-Pd combinations. However for the Pd-Ru catalysts, the reflections due to Pd rich alloy phases and from unalloyed Ru were observed separately. Pd-Ru does not form solid solution in the composition range 20-80 atom% Ru [31]. The crystallite size values, the metal surface area (MSA) and dispersion (D in%) values catalysts have been described in Table I. The lattice constant values were calculated using the formula for the FCC structure of the alloy and also indicated. Chemical reduction method usually results in P crystallites with smaller particle size than incipient reduction method [27]. This is true with Pt- Ru, Pt-Pd and Pd-Ag catalysts. Heat treatment results in agglomeration of smaller particles and higher crystallite size. However for Pd-Ru catalysts, the reverse trend is observed similar to the behaviour reported for Pd catalyst [32]. The lattice constant values also shift according to the phenomena reported for a FCC solid solution. From the shift of the lattice constant value the composition of the binary phase can be calculated.

Electrochemical characterisation of the catalysts

The cathodic oxide reduction peak potential in the cyclic voltammograms is reported to show a linear dependence of the surface composition of the binary Pt-Pd alloy catalyst

TABLE II: Electrochemical characteristics of bimetallic supported catalysts

Catalyst	Bulk Composition atom %	atom %	Method	Q_{o2} C/g	ESA m^2/g	Surface Composition atom %	atom %	Dispersion D=H/M	C_s nm
Pt-Pd	80	20	chemical	12.78	60.80	84	16	24	4.60
Pt-Pd	60	40	"	13.68	65.10	72	28	25	4.30
Pt-Pd	50	50	"	8.65	70.10	65	35	27	4.00
Pt-Pd	40	60	"	11.48	90.30	53	47	35	3.10
Pt-Pd	20	80	"	14.80	93.30	35	65	38	3.30
Pt-Pd	50	50	incipient	13.61	68.20	74	24	30	3.80
Pt-Ru	50	50	chemical	12.70	30.40	70	30	12	8.80
Pt-Ru	50	50	incipient	9.10	21.50	75	25	8	13.00
Pd-Ru	75	25	"	9.02	49.10			11	10.20
Pd-Ru	50	50	"	7.46	38.20			8	13.10
Pd-Ru	25	75	"	7.91	40.00			8	12.50
Pd-Ru	50	50	chemical	10.10	45.05			11	9.70
Pd-Ru	50	50	heat treated	6.37	26.30			7	14.70

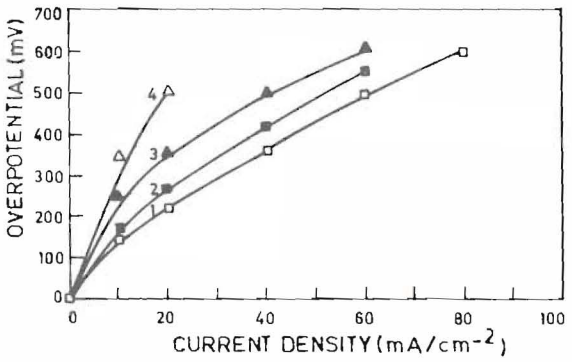

Fig. 1: Polarisation curves for Pt-Pd/C catalysts for methanol oxidation in 1 M H_2SO_4
(1) Pt-Pd (80:20 atom %) (2) Pt-Pd (60:40 atom %)
(3) Pt-Pd (40:60 atom %) (4) Pt-Pd (20:80 atom %)

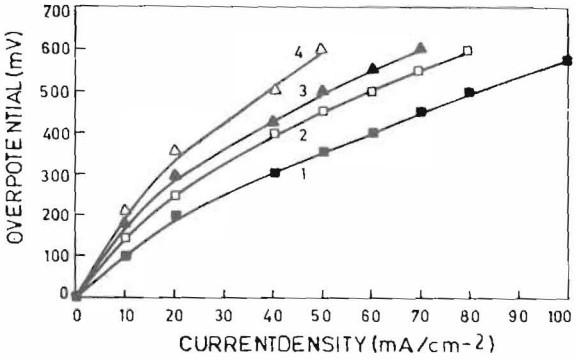

Fig. 2: Polarisation curves for Pt-Pd/C catalysts for methanol oxidation in 1 M KOH
(1) Pt-Pd (80:20 atom %) (2) Pt-Pd (60:40 atom %)
(3) Pt-Pd (40:60 atom %) (4) Pt-Pd (20:80 atom %)

[33]. The electrochemical surface area of the binary catalysts, the crystallite size and dispersion values calculated therefrom are indicated in Table II. For Pt-Pd catalysts, the surface composition is richer in Pt in a similar fashion reported for Pt- Ru catalyst [28]. The crystallite size values decrease as the Pd content increases in the binary phase. The size of the bimetallic catalysts is comparatively bigger than the corresponding monometallics. No correletaion of the oxide reduction potential was noticed with Pd Ru catalysts. The electrochemical surface area values are higher than the values reported earlier under Table I. The crystallite size values of Pd alloy catalysts prepared by incipient method are less than the catalysts prepared by incipient method. It is also found that the crystallite size bears no direct relationship with the composition of the Pt-Pd binary catalysts.

Electrocatalytic activity of the binary catalysts

Polarisation curves were obtained with Pt-Pd/C catalysed electrodes in acid and alkaline medium for the oxidation of methanol and the results are shown in Figs. 1 and 2 respectively. It is found that the polarisation values are minimum at higher Pt contents in the bimetallics and increase with the Pd content for methanol oxidation in acid and alkaline medium. In alkaline medium, generally high current density values are noticed at any polarisation values compared to that in acid medium.

Since the electrochemical surface area values determined as above are different for different catalysts, the specific catalytic activity values are calculated per unit real surface area of the catalyst. Table III indicates the sp. activity values obtained in acid and alkaline medium. Comparisons have been made at an overpotential of 500 mV. From the table it is clear that the sp. activity values decrease as the Pd content increases in the alloy catalysts. The sp. activity values maximum is realised when the dispersion values are higher. The maximum catalytic activity has been noticed for 20 atom% Pd containing catalysts corresponding to a surface composition of 16 atom%.

The specific activity values obtained with oxidation of formaldehyde and ethylene glycol are also indicated in Table III. Generally Pt-Pd catalysts were found to be less active towards oxidation of formaldehyde than with methanol or glycol. However the sp. activity values were higher in alkaline medium than observed in acid medium. A steady activity decrease has been noticed in acid medium when the Pd content increases. In contrast to this, an activity maximum has been observed in alkaline medium at 60:40 for formaldehyde and at 50:50 for ethylene glycol oxidation. The catalysts prepared by the chemical reduction methods exhibit a higher activity than when prepared by impregnation method.

The sp. activity values for Pt-Pd catalysts were lower than the values reported earlier for Pt-Ru/C catalysts [28]. It is reported that Pt-Ru/C catalysts have an activity maximum for methanol oxidation in acid medium at a bulk composition of Pt:Ru (60:40), which is reported to have a surface composition of 75:25 atom%. Activity comparisons have also been made for Pt-Ru catalysts for the oxidation reactions in alkaline medium as shown in Fig. 3. The activity values for formaldehyde and glycol were less than methanol in acid and alkaline medium. In alkaline medium the activity for

TABLE III: Comparison of specific activity of bimetallic catalysts

Catalyst	Bulk Composition		methanol		formaldehyde		ethylene glycol	
	Pt (at%)	Pd (at%)	(A/g)	(A/m^2)	(A/g)	(A/m^2)	(A/g)	(A/m^2)
Acid medium								
Pt-Pd	80	20	30.00	0.490	10.0	0.16	21.0	0.34
	60	40	27.00	0.400	10.0	0.14	17.5	0.26
	50	50	21.00	0.300	9.0	0.12	13.5	0.18
	40	60	12.00	0.140	6.0	0.06	8.0	0.08
	20	80	5.00	0.060	4.0	0.04	5.0	0.06
Pt-Ru	50	50	50.00	1.640	6.4	0.21	11.3	0.37
incipient	50	50	15.00	0.690	4.1	0.19	3.0	0.14
Pd-Ru	75	25	2.20	0.020				
	50	50	1.20	0.020				
	25	75	0.35	0.004				
incipient	50	50	1.30	0.010				
heat treated	50	50	0.80	0.002				
Alkaline medium								
Pt-Pd	80	20	32.50	0.520	12.5	0.20	25.0	0.40
	60	40	31.00	0.440	16.5	0.25	30.0	0.46
	50	50	20.00	0.330	15.0	0.21	40.0	0.57
	40	20	12.00	0.140	14.0	0.14	18.5	0.21
	20	80	7.00	0.080	11.0	0.12	15.0	0.16
Pt-Ru	50	50	30.00	0.990	10.9	0.36	12.8	0.42
incipient	50	50	6.80	0.170	12.5	0.33	11.8	0.39
Pd-Ru	75	25	17.00	0.170	21.0	0.22	27.0	0.27
	50	50	15.00	0.170	25.0	0.33	30.0	0.39
	25	75	8.50	0.100	11.0	0.14	75.0	0.18
incipient	50	50	16.00	0.180	30.0	0.33	34.0	0.36
heat treated	50	50	9.00	0.170	15.0	0.28	17.0	0.32

glycol oxidation is higher than formaldehyde. It seems Pt-Ru catalysts are selective towards methanol oxidation reaction.

Fig. 4 shows the specific activity composition relationship for Pd-Ru catalysts. A maximum in the relationship has been observed for the catalyst, which has a composition of 75 atom% Pd (bulk) for methanol in acid medium and

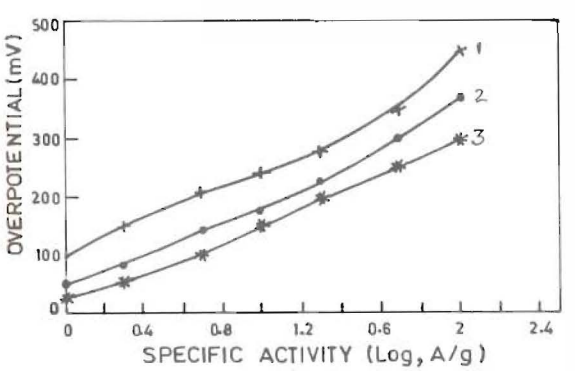

Fig. 3: Polarisation-specific activity data for Pt-Ru/C catalysts in 1 M KH with HCHO and glycol
(1) Pt-Ru (80:20 atom %) HCHO
(2) Pt-Ru (60:40 atom %) for HCHO
(3) Pt-Ru (80:20 atom %) for glycol

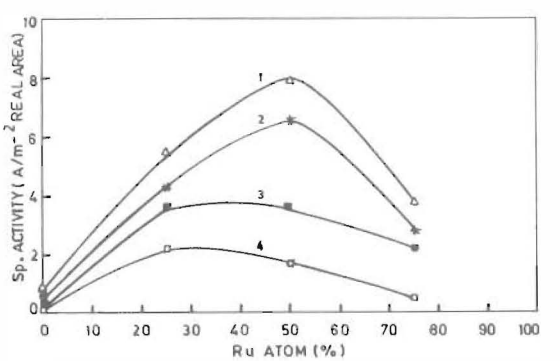

Fig. 4: Comparison of sp activity of Pd-Ru/C catalysts in acid and in alkaline medium
(1) Glycol in alkali (2) HCHO in alkali
(3) methanol in alkali (4) methanol in acid

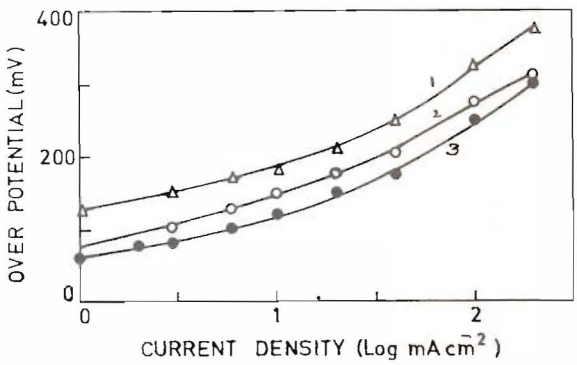

Fig. 5: Tafel plots for the oxidation of formaldehyde in 1 M KOH with Pd-Ag/C catalysts (1) Pd-Ag (75:25 atom %) (2) Pd-Ag (50:50 atom %) (3) Pd-Ag (75:25 atom %)

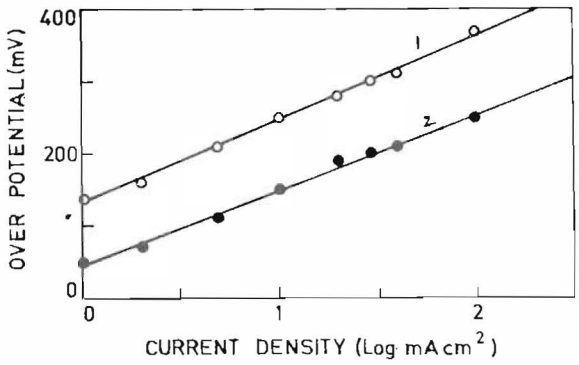

Fig. 6: Tafel plots for the oxidation of ethylene glycol in 1 M KOH with Pd-Ag catalysts (1) Pd-Ag (75:25 atom %) (2) Pd-Ag (50:50 atom %)

50 atom% Ru for the oxidation of formaldehyde and ethylene glycol in alkaline medium. The practical current density values are found to be lower than the Pt-Ru catalysts. But the sp. activity values in alkaline medium are comparable with Pt-Pd catalysts. The activity values were independent upon the method of preparation viz. chemical or dry reduction technique.

The electrocatalytic oxidation of methanol, formaldehyde and ethylene glycol on Pd-Ag catalysts was also studied in alkaline medium. Methanol was not oxidised on Pd-Ag catalysts. However the current due to oxidation of HCHO and ethylene glycol are found to be increased in alkaline medium. Figs. 5 and 6 show the polarisation curves for the oxidation of HCHO and glycol in alkaline medium. The catalyst system exhibited a rest potential of -1050 mV vs MOE very quickly, which is very close to the theoretical reversible potential values of -1100 mV of HCHO/CO_3^{2-} couple [34]. The attainment of the equilibrium potential close to the theoretical reversible value is an indication of the applicability of the system as a promising electrocatalyst for the oxidation of these compounds. The Pd-Ag catalyst exhibited an activity maximum at 50 atom% Ag for the oxidation of ethylene glycol. The synergistic effect is very similar to the behaviour reported for Pt-Pd alloys [35] and Pd-Au alloys [36] in alkaline medium. The current density values on Pd-Ag alloys are higher than Pt-Pd alloys. From the above plots a tafel slope of 130 mV is obtained for glycol oxidation on Pd-Ag catalysts. The value is very close to the value of 110 mV reported for Pt [37] and 120 mV for Pd [38].

CONCLUSION

Pt-Pd catalysts were found to be less active towards oxidation of formaldehyde than with methanol or glycol in acid and alkaline medium. However the sp. activity values were higher in alkaline medium than in acid medium. A steady activity decrease has been noticed in acid medium when the Pd content increases. In contrast to this, an activity maximum has been observed in alkaline medium for the oxidation of formaldehyde and glycol. The surface area and hence the electrochemical activity depend upon the method of preparation of the catalyst. Pd-Ru catalysts were found to be less active than Pt-Pd catalysts. The current density values on Pd-Ag alloys were higher than Pt-Pd alloys and a synergism was noticed at 50 atomic% composition.

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